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(54) **NOUVEAUX MATERIAUX D'ELECTRODE PRESENTANT UNE CONDUCTIVITE DE SURFACE ELEVEE**

(54) **NEW ELECTRODE MATERIALS WITH HIGH SURFACE CONDUCTIVITY**

(57) The present invention concerns The present invention concerns [sic] electrode materials capable of redox reactions by exchanging alkaline ions and electrons with an electrolyte. Applications are in the fields of primary and secondary electrochemical generators (batteries), supercapacitors and supercapacitor-type light modulation systems.

[image]   Industrie Canada   Industry Canada

TITLE

New electrode materials with high surface conductivity

SCOPE OF THE INVENTION

The present invention concerns electrode materials capable of redox reactions by exchanging alkaline ions and electrons with an electrolyte. Applications are in the fields of primary and secondary electrochemical generators (batteries), supercapacitors and supercapacitor-type light modulation systems.

PRIOR ART

Prior art gives insertion compounds (hereinafter also called electroactive materials or redox materials) which operate through the exchange of alkaline ions, lithium ions in particular, and valence electrons of a transition element, such as to provide neutrality in a solid matrix. The partial or total preservation of structural integrity in the material allows for the reversibility of the reaction. It is also possible to obtain solid phase reactions through the reversible break-up of sulfur-sulfur bonds, or through redox reactions which occur in the transformation of aromatic organic structures into quinonic forms, particularly in conjugated polymers.

Insertion materials are the active ingredients in electrochemical reactions which occur in particular in electrochemical generators, supercapacitors, and light transmission modulation systems (electrochromatic systems).

The progress of the ion-electron exchange reaction requires the existence within the insertion material of a double conductivity, both electronic and ionic, in particular for lithium ions; either one of these conductivity types may be too weak to ensure the exchange kinetics required for the use of these materials, in particular for electrochemical generators and supercapacitors. One solution to this problem is partially obtained by the use of so-called "composite" electrodes, wherein the electrode material is dispersed in a matrix containing the electrolyte and a polymer binder. Where the electrolyte is a polymer electrolyte or a gel functioning in the absence of a solvent, the role of the mechanical binder is played directly by this material. Gel is understood to be a polymer matrix, itself solvating or not, retaining a polar liquid and a salt such as to provide the compound with the mechanical properties of a solid while preserving at least part of the conductivity of the polar liquid. A liquid electrolyte and the electrode material may also be maintained in contact by using a small fraction of an inert polymer binder, i.e. not interacting with the solvent. Using any of the aforementioned means, each grain of the electrode material is enveloped in an electrolyte capable of bringing the ions in direct contact with virtually the entire surface of the electrode material. To facilitate electron exchanges, prior art gives the common approach of adding to one of the aforementioned mixtures of electrode material and electrolyte, particles of a conducting material in a very divided state. Generally, carbonaceous materials are the choice, particularly acetylene black (Shawinigan or Ketjenblack®). However, the volume fractions employed are low seeing as this type of material significantly alters the rheology of polymers, resulting in excessive

porosity and a loss of operating efficiency in the composite electrode, both in terms of share of usable capacity, and kinetics, i.e., available power. With the low concentrations employed, the grains of carbon become structured into chains, and the points of contact with the electrode material as such are extremely reduced. This configuration results in an improper distribution of the electrical potential within the electroactive material. In particular, overconcentration or depletion may occur at triple junction points:
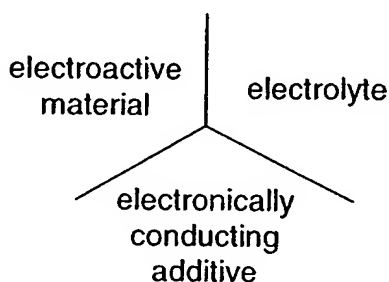
These abnormal variations in the local concentration of mobile ions and the gradients resulting within the electroactive material severely impair the reversibility of the electrode operating over a large number of cycles. These chemical and mechanical constraints (stress) translate at a microscopic scale into the disintegration of grains of electronegative material, a portion of which are likely to lose contact with the grains of carbon and thus be rendered electrochemically inactive. The structure of the material may then become degraded, as new phases emerge and ions of transition metal are potentially salted out into the electrolyte. The occurrence of such harmful effects is further encouraged when significant current density and power are required at the electrode.

DETAILED DESCRIPTION OF THE INVENTION

The present invention enables the manufacture of electrode materials of an extremely varied composition characterized by having their surface, or the most part of their surface, covered in an even coating of conducting carbonaceous material deposited through chemical means. The presence in the compounds as per the invention of an even coating as opposed to the punctual contact obtained with the carbon powders and other conducting additives from prior art, provides an even distribution of the electric field across the surface of the grains of electroactive material, while significantly diminishing ion concentration gradients. This improved distribution of electrochemical reaction at the surface of particles preserves, on one hand, the structural integrity of the material, and, on the other hand, improves the kinetics, in terms of current density and power available at the electrode, in view of the larger surface available.

[figure]   [figure]

a)   b)

Diagram 1 illustrates the difference between a classical electrode given by prior art (a) and an electrode as per the invention wherein particles of electroactive material are covered in a carbonaceous coating (b).

Carbonaceous material is understood to be a polymer comprising carbon for the most part, between 60% and 100% molar, and exhibiting electronic conductivity greater than 10^{-5} Scm^{-1} at regular temperatures, preferably greater than 10^{-3} Scm^{-1}. The other elements present may be hydrogen, oxygen, or nitrogen; these do not interfere with the chemical inertia characteristic to carbon.

Improved conductivity at the surface of the grains, obtained by the carbonaceous material coating, provides a satisfactory operation of electrodes containing electroactive materials whose electronic conductivity is insufficient for acceptable performance. The choice of structures or phase mixtures exhibiting redox properties while having low electronic conductivity is much wider than that of compounds from prior art (mixed oxide of transition metals and lithium). In particular, redox structures may include elements chosen among non-metals (metalloids), such as sulfur, selenium, phosphorus, arsenic, silicon and germanium, with a higher electronegativity which enables the redox potential of transition elements to be modulated – however, at the expense of electronic conductivity. A similar effect is obtained by a partial or total substitution of oxygen atoms with fluoride or nitrogen.

Redox materials are thus described by the general formula $A_aM_mZ_zO_oN_nF_f$ where:

A is an alkaline metal chosen among Li, Na, K;

M is a transition metal;

Z is a non-metal chosen among S, Se, P, As, Si, Ge, Sn;

O is oxygen;

N is nitrogen and F is fluoride; the latter elements may be substituted for oxygen in the complex oxide due to the ionic radii similar to those of F^-, O^{2-} and N^{3-} ions; and

the coefficients a, m, z, o, n, f $\geq$ 0 are chosen such as to provide electroneutrality.

The carbonaceous coating may be deposited using various techniques, which are an integral part of the invention. A preferred method is to pyrolyze an organic material, preferably rich in carbon, in the presence of a redox material. Mesomolecules and polymers likely to form an even coating on the surface of the grains of redox materials, either mechanically; through impregnation using a solution; or through *in situ* polymerization, are particularly suitable, as their pyrolysis produces a thin and even coating of carbonaceous material on the surface of the grains. To prevent the composition of the redox material from being affected by the pyrolysis reaction, it is sensible to choose compositions wherein the pressure of oxygen released by the material is sufficiently low such as to avoid oxidation of the carbon formed during pyrolysis. Oxygen activity in $A_aM_mZ_zO_oN_nF_f$ compounds can be controlled through the alkaline metal content, which determines the state of oxidation of the transition element or elements contained in the material and is an integral part of the invention. Compositions determined by the coefficient "a" describing the alkaline metal content, capable of maintaining the following oxidation states: Fe^{2+}, Mn^{2+}, V^{2+}, V^{3+}, Ti^{2+}, Ti^{3+}, Mo^{3+}, Mo^{4+}, Nb^{3+}, Nb^{4+}, W^{4+}, are particularly interesting. Generally, oxygen pressures on the order of 10^{-20} bar at 0°C and 10^{-10} bar at 900°C are sufficiently low to allow carbon deposits through pyrolysis; the kinetics of carbon formation in the presence of hydrocarbon residue from pyrolysis is faster and less

activated than oxygen formation from redox materials. It is also possible and beneficial to choose materials where oxygen pressure in equilibrium with the material is below that of the equilibrium

$$C + O_2 \Leftrightarrow CO_2$$
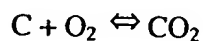
In this case, the carbonaceous material may be thermodynamically stable with regard to the complex oxide. The corresponding pressures are given by the following formula:

$$\ln P(O_2) = \ln P(CO_2) = \frac{94050}{R(273.2 + \theta)}$$

where R is the ideal gas constant (1.987 cal·mole^{-1}·K^{-1}); and

θ is the temperature in °C.

The following table gives oxygen pressure values for several temperatures:

θ (°C)		200	300	400	500
$P(CO_2) = 1$ Atm	$P(O_2)$	3.5×10^{-44}	1.4×10^{-36}	2.9×10^{-31}	2.5×10^{-27}
$P(CO_2) = 10^{-5}$ Atm	$P(O_2)$	3.5×10^{-49}	1.4×10^{-41}	2.9×10^{-36}	2.5×10^{-32}

θ (°C)		600	700	800	900
$P(CO_2) = 1$ Atm	$P(O_2)$	2.9×10^{-24}	7.5×10^{-22}	7.0×10^{-20}	3.0×10^{-18}
$P(CO_2) = 10^{-5}$ Atm	$P(O_2)$	2.9×10^{-29}	7.5×10^{-27}	7.0×10^{-25}	3.0×10^{-23}

The carbonaceous coating may also be obtained through disproportionation of the carbon oxide at temperatures below 800°C according to the equation:

$$2CO \Rightarrow C + CO_2$$
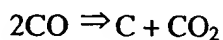
This reaction is exothermic but slow. Particles of complex oxide can be brought into contact with carbon monoxide, in pure form or diluted with an inert gas, at temperatures ranging from 100 to 750°C, preferably 300 to 650°C. It is beneficial if the reaction is conducted in a fluidized bed technique, such as to provide a large exchange surface between the gaseous phase and solid phase. The elements and cations of transition metals act as catalysts in the disproportionation reaction. It must be noted that these elements are present in the complex oxide. It may be interesting to add small amounts of iron, nickel or cobalt salts to the surface of the grains; these elements are particularly active as catalysts in the disproportionation reaction.

In one version, the deposit of carbonaceous material may be obtained simultaneously with a variation in the content of alkaline metals A. For this purpose, a salt of an organic acid or polyacid is mixed with the complex oxide. Another possibility is to begin with a monomer or a monomer mixture which is polymerized *in situ*. During pyrolysis, the compound deposits a film of carbonaceous material onto the surface and the alkaline metal A is incorporated according to the equation:

$$A_{a'}M_mZ_zO_oN_nF_f + A_{a-a'}C_cO_oR' \Rightarrow A_aM_mZ_zO_oN_nF_f$$
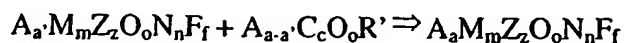
R' being a particular organic radical, potentially part of a polymer tar.

Among the compounds likely to allow this reaction, examples without limitation include salts of carboxylic acids such as salts of the oxalic, malonic, succinic, citric, polyacrylic, polymethacrylic, benzoic, phthalic, propiolic, acetylene dicarboxylic, naphthalene di- or tetracarboxylic, perylenetetracarboxylic, and diphenic acids.

It is evident that the pyrolysis of an organic material which does not contain an alkaline element and the provision of the latter by means of a salt may be combined in order to arrive at the desired stoichiometry of the complex oxide.

It is also possible to obtain a deposit of material, particularly at low or average temperatures, below 400°C, through a reduction of carbon-halogen bonds according to the equation:

$$CY\text{-}CY + 2e^- \Rightarrow \text{-}C\text{=}C\text{-} + 2Y^-$$
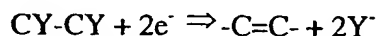
where Y is a halogen or a pseudo-halogen. Pseudo-halogen is understood to be an organic or inorganic radical likely to exist in the form of a Y^- ion and to form the corresponding protonated compound HY. Among the halogens and pseudohalogens, examples include without limitation F, Cl, Br, I, CN, SCN, CNO, OH, N_3, RCO_2, RSO_3 where R represents H or an organic radical. The formation of the CY bond is benefited by the presence of reducing elements, including zinc, magnesium, the ions Ti^{3+}, Ti^{2+}, Sm^{2+}, Cr^{2+}, V^{2+}, tetrakis(dialkylaminoethylene), and phosphines. These reagents may be obtained or regenerated electrochemically. Among others, it may be beneficial to employ catalysts to increase reaction kinetics. Derivatives of palladium or nickel

are especially effective, in particular as complexes with phosphines or nitrogen compounds such as 2,2'-bipyridine. Likewise, these compounds may be generated in active form, either chemically in the presence of reducers, in particular those mentioned above, or electrochemically. Among the compounds likely to generate carbon through reduction, examples include perhalocarbons, in particular as polymers, hexachlorobutadiene, and hexachlorocyclopentadiene.

Another low-temperature approach to releasing carbon is to eliminate the hydrogenated compound HY, Y being such as defined above, according to the equation:

$$-CH-CY- + B \Rightarrow -C=C- + BHY$$

Among the compounds likely to generate carbon through reduction, examples include organic compounds comprising an equivalent number of hydrogen atoms and Y groups, such as hydrohalocarbons, particularly in the form of polymers, such as polyvinylidene fluoride, chloride, bromide or acetate, and carbohydrates. Dehydro(pseudo)halogenation can be obtained at low temperature, including room temperature, using a base likely to react with the HY compound to form a salt. For this purpose, suitable examples include tertiary, amine, amidine, guanidine, imidazole bases, inorganic bases such as alkaline hydroxides, organometallic compounds acting as strong bases; possible examples are $A(N(Si(CH_3)_3)_2$, $LiN[CH(CH_3)_2]_2$, and butyl lithium.

In the latter two methods cited, it may be beneficial to anneal the materials following the carbon deposit. This treatment enhances the structure or the crystallinity of the carbon. The treatment may be conducted at 100 to 800°C, preferably 100 to 400°C, to avoid a potential reduction of the complex oxide by the carbonaceous material.

As a general rule, it is possible to obtain even coatings of carbonaceous material with sufficient electronic conductivity, i.e. at least of the same order as the ionic conductivity within the grain of oxide. Thick coatings allow for a conductivity sufficient for the binary mixture of grains of complex oxide enveloped in carbonaceous material with the electrolyte, liquid or polymer, or the macromolecular inert binder due to be imbued in electrolyte, to be conducting by simple contact between the particles. In general, this behavior can be observed with volume fractions between 10% and 70%.

It may also be beneficial to choose deposits of sufficiently fine carbonaceous material such as not to obstruct the passage of ions, while ensuring the distribution of electrochemical potential over the surface of the grain. In this case, binary mixtures may not have sufficient electronic conductivity to ensure electron exchanges with the electrode support (current collector). Adding a third electronically conducting component, in the form of a fine powder or fibers, allows a satisfactory macroscopic conductivity and enhances electron exchanges with the electrode support. Carbon black and carbon fibers are particularly suited for this purpose, and offer

satisfactory results, at volumes not affecting or affecting to a little extent rheology when operating the electrode, due to the existence of electronic conductivity at the surface of the grains of electrode material. Volume fractions between 0.5% to 10% are particularly preferred. Carbon black such as Shawinigan® or Ketjenblack® is preferred. Among carbon fibers, those obtained through pyrolysis of polymers such as tar, polyacrylonitrile, as well as those obtained by hydrocarbon cracking, are preferred.

Due to its light weight and malleability, aluminum is an interesting option as a constituent of current collectors. However, this metal is covered in an insulating oxide layer. This layer, which protects the metal from corrosion, may under some circumstances add to overall thickness, increasing resistance at the interface and hampering the proper operation of the electrochemical cell. This phenomenon can be particularly harmful and fast-setting in cases where electronic conductivity is solely provided, as in prior art, by grains of carbon with a limited number of contact points. The use, in conjunction with aluminum, of electrode materials covered in a layer of conducting carbonaceous material allows for an increased aluminum-electrode exchange surface. The effects of aluminum corrosion are thus eliminated or at least minimized. It may be possible to use aluminum collectors shaped as strips or in expanded form, thus allowing for weight savings. Given the properties of the materials as per the invention, even in the case of expanded metal, electron exchanges at the collector level occur without a notable rise in resistance.

In cases where the current collectors are thermally stable, it is also possible to conduct pyrolysis directly on the collector, such as to obtain, after the carbon is deposited, a continuous porous layer which may be infiltrated with an ionically conducting liquid, or with a monomer or monomer mixture whose *in situ* polymerization generates a polymer electrolyte. Porous films wherein the carbonaceous coating forms a tar are easily obtained under the invention through the pyrolysis of a complex polymer-oxide composite deposited as a film onto a metallic support.

While the present invention has been described as being aimed at specific implementations, it is understood that several variations and modifications may be brought to said implementations, and the present application covers those modifications, uses or adaptations of the present invention which generally follow the principles of the invention and include any variation of the present description which will become known or commonplace in the field of activity specific to the present invention, and which may apply to the essential elements mentioned above, in accordance with the scope of the following claims.

CLAIMS

1. Single- or multiphase-type electrode material comprising a complex oxide corresponding to the general formula $A_aM_mZ_zO_oN_nF_f$ where:

A is an alkaline metal chosen among Li, Na, K;

M is a transition metal;

Z is a non-metal chosen among S, Se, P, As, Si, Ge, Sn;

O is oxygen; N is nitrogen and F is fluoride; and

the coefficients a, m, z, o, n, f $\geq$ 0 are chosen such as to provide electroneutrality, characterized in that a layer of carbonaceous material is evenly deposited onto a surface through chemical means.

2. Material as per claim 1, characterized in that the carbonaceous deposit is obtained through pyrolysis of an organic material, particularly a polymer.

3. Material as per claim 1, characterized in that the value of the coefficient "a" is selected for the carbonaceous coating such that the oxygen pressure in equilibrium with the material is below 10^{-20} at 0°C and 10^{-10} at 900°C.

4. Material as per claim 3, characterized in that the oxygen pressure in equilibrium with the material is below the oxygen pressure corresponding to the equilibrium $C + O_2 \Leftrightarrow CO_2$ in the temperature range between 100 and 900°C, preferably between 200 and 750°C.

5. Material as per claims 1 to 4, characterized in that transition elements are present in the following states of oxidation: Fe^{2+}, Mn^{2+}, V^{2+}, V^{3+}, Ti^{2+}, Ti^{3+}, Mo^{3+}, Mo^{4+}, Nb^{3+}, Nb^{4+}, W^{4+}.

6. Material as per claim 1, characterized in that the precursor of the carbonaceous material is a polymer.

7. Material as per claim 6, characterized in that the polymer is chosen among polyolefins, polybutadienes, polyvinyl alcohol, phenol condensates, including those with condensed cores, with formaldehyde, polymers derived from furfuryl alcohol, polymers derived from styrene, divinylbenzene, acrylonitrile, vinyl acetate, cellulose, starch and its esters.

8. Depositing technique for the conducting carbonaceous material as per claim 6, characterized in that the polymer or polymer mixture is dispersed with the complex oxide $A_aM_mZ_zO_oN_nF_f$ either mechanically in a solid state or using a solution containing the polymer or polymer mixture and the solvent, evaporated or diluted in a nonsolvent of the polymer or polymers, and in that pyrolysis is conducted in a vacuum or in a non-reactive atmosphere such as helium, argon, nitrogen, or carbon dioxide.

9. Depositing technique for the conducting carbonaceous material as per claim 6, characterized in that a monomer or monomer mixture is added to the complex oxide $A_aM_mZ_zO_oN_nF_f$ mechanically in a solid state or using a solution, followed

by a polymerization, and in that pyrolysis is conducted in a vacuum or in a non-reactive atmosphere such as helium, argon, nitrogen, or carbon dioxide.

10. Depositing technique for the conducting carbonaceous material as per claim 1, characterized in that the source of carbon is carbon monoxide CO alone or in a mixture with an inert gas, and in that the deposit is obtained through the equilibrium of the disproportionation $2\ CO \Rightarrow C + CO_2$ at a temperature below 900°C, preferably below 750°C, potentially in the presence of a catalyst such as a derivative of iron, cobalt, or nickel.

11. Depositing technique for the conducting carbonaceous material as per claim 1, characterized in that it is obtained at a low temperature, preferably below 250°C, and in that the source of carbon is an organic compound which produces this element through the reduction of CY bonds or through elimination of the HY hydrogenated compound, where Y represents a halogen or pseudo-halogen.

12. Depositing technique for the conducting carbonaceous material as per claim 11, characterized in that the reduction of CY bonds occurs in the presence of a catalyst such as a palladium or nickel complex with phosphines or aza-aromatic compounds such as bipyridines, or in that the elimination of HY is obtained thermally or catalyzed by an organic base.

13. Depositing technique for the conducting carbonaceous material as per claim 11, characterized in that Y comprises Cl, Br, RCO_2, RO where R is an organic group of 1 to 8 carbon atoms.

14. Preparation technique for the electrode material as per claim 1, characterized in that the deposit is obtained through pyrolysis from an organic derivative of an alkaline metal A providing the a-a' fraction of alkaline metal from the complex oxide $A_{a'}M_mZ_zO_oN_nF_f$ such as to obtain through pyrolysis a carbonaceous deposit on the surface of the complex oxide whose composition becomes $A_aM_mZ_zO_oN_nF_f$, such that a-a' > 0.

15. Material as per claim 1, characterized in that the final content of carbonaceous material is comprised between 0.1 and 55% by weight.

16. Material as per claim 15, characterized in that the final content of carbonaceous material is comprised between 0.2 and 15% by weight.

17. Material as per claim 1, characterized in that it comprises a complex oxide chosen among sulfates, phosphates, silicates, oxysulfates, oxyphosphates, oxysilicates or their double mixtures with a transition metal and lithium, their mixtures or solid solutions.

18. Material as per claim 1, characterized in that it corresponds to the general formula $Li_{1+x}MP_{1-x}Si_xO_4$ or $Li_{1+x-y}MP_{1-x}Si_xO_{4-y}F_y$ where $0 \leq x, y \leq 1$ and M comprises Fe or Mn.

19. Material as per claim 1, characterized in that the complex oxide corresponds to the general formula $Li_{3-x+z}M_2(P_{1-x-z}S_xSi_zO_4)_3$ where M and x are such as previously defined, and $z \leq 1$.

20. Material as per claim 1, characterized in that the complex oxide corresponds to the general formula $Li_{3+u-x+z}V_{2-z-w}Fe_uTi_w(P_{1-x-z}S_xSi_zO_4)_3$ where $0 \leq x$; $w \leq 2$; $0 \leq x$ and $z \leq 1$.

21. Electrochemical cell characterized in that at least one electrode comprises at least one material as per claim 1.

22. Electrochemical cell as per claim 21 characterized in that it operates as a primary or secondary battery, supercapacitor, or electrochromatic light modulation system.

23. Cell as per claim 22 which is a primary or secondary battery, characterized in that the electrode is a polymer, solvating or not, potentially plasticized or gelled by a polar solvent containing in solution one or more metallic salts, in particular, a lithium salt.

24. Cell as per claim 22 which is a primary or secondary battery, characterized in that the electrolyte is a polar liquid immobilized within a microporous separator, in particular a polyolefin, a polyester, nanoparticles of silica, alumina or lithium aluminate $LiAlO_2$.

25. Cell as per claim 23 or 24 wherein one of the metallic salts is a lithium salt.

26. Cell as per claim 23 which is a primary or secondary battery, characterized in that the polymer comprising a salt and potentially a polar liquid is formed from oxyethylene, oxypropylene, acrylonitrile or vinylidene fluoride units, esters of acrylic or methacrylic acid, esters of itaconic acid with alkyl or oxyalkyl groups, particularly derivatives of ethylene oxide.

26 [sic]. Cell as per claim 23, 24, 25 or 26 characterized in that the polar liquid is chosen among cyclic or linear carbonates, alkyl formate, alpha-omega ethers of oligoethylene glycols, N-methylpyrrolidinone, gamma-butyrolactone, tetra-alakylsulfamides and mixtures thereof.

27. Cell as per any of claims 21 to 26 wherein the current collector of the electrode containing the electrode material is made of aluminum, potentially in the form of expanded metal.

ABSTRACT

The present invention concerns electrode materials capable of redox reactions by exchanging alkaline ions and electrons with an electrolyte. Applications are in the fields of primary and secondary electrochemical generators (batteries), supercapacitors and supercapacitor-type light modulation systems.